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THERMOPHYSICAL PROPERTIES OF SOME SELECTED ALTERNATIVE REFRIGERANTS

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ABSTRACT

A summary of a thermophysical properties program for six candidate alternative refrigerants is given. This work has been performed recently at the National Institute of Standards and Technology (U.S.A.), Thermophysics Division, in Gaithersburg, Maryland. Properties measured include gas and liquid-phase PVT, vapor pressures, surface tension, index of refraction, dielectric constant, gas phase speed of sound, critical parameters and materials compatibility. Results have been obtained for R 123, R 125, R 134, R 134a, R 141b, and E 134 (some properties only).

INTRODUCTION

The ASHRAE 1989 CFC Technology Conference was held at the NIST laboratories in Gaithersburg MD in September 1989. There, it was pointed out that published information on the thermophysical properties of the potential alternative refrigerants was at best spotty and in many cases, nonexistent. Only for R 134a and several mixtures do the published measurements approach those available for the present refrigerants. For R 123 the lack of publications was particularly notable. The information reported on the others is of mixed quality; some of it would be of limited usefulness for the calculation of accurate thermodynamic properties. This assessment does not, however, reflect the level of experimental effort being expended on these measurements worldwide. Due to the normal delays which occur between measurement and publication, much of this work has not appeared in print. This paper gives a brief survey of the experimental measurements that have been made in the Thermophysics Division at NIST in Gaithersburg, Maryland during the past two years. Some of this work has been published, but much remains unpublished at present. Although I will concentrate on my own measurements, on R 134a, R 123 and R 141b, I will show some typical examples of the other results from our group, particularly where they overlap or complement my work.

MEASUREMENTS

The Gaithersburg portion of the Thermophysics Division has a wide variety of experimental capabilities, many of which have been turned to measurements on refrigerants. The Appendix gives a brief summary of each apparatus along with its operating range and its accuracy. Some results can be obtained relatively quickly, and the number of systems studied has gone far beyond the leading three candidates which have been measured in the slow, classical gas-phase PVT apparatus. Not all of the results are comprehensive, however, that is they do not yet cover the whole range of pressure and temperature of interest. The compressed liquid PVT measurements are at present limited to $T < 373$ K; the index of refraction measurements were made on saturated liquid and vapor only; speed of sound has been measured for the gas phase at temperatures below 65°C for R134a and R123 and below 40°C for R141b; dielectric constant has been measured only in the gas phase. The compatibility tests were of the sealed ampule type. They were used to determine compatibility with various metals at elevated temperatures, [1]. The measurements which we make, that are applicable to refrigerants, are as follows.

The index of refraction, n , can be used to calculate the density by means of the Lorenz-Lorentz relationship:

$$(n^2 - 1)/(n^2 + 2) = A \rho \quad (1)$$

which holds surprisingly well. The value of A (the molecular polarizability) can

be determined from a calibration point (eg. the saturated liquid density at room temperature). This relationship is only approximately true, but in practice A varies only about 1% with density and hardly at all with temperature. This technique has been used to determine the polarizability and densities at saturation at elevated temperatures, as well as critical densities and temperatures of several refrigerants, ref.[2-4]. Measurements are made in an optical cell, with sapphire windows, by measuring the angle of refraction of a laser beam by a prism. An example of the results is shown in figure 1 for R 141b.

Dielectric constant behavior is described by the Clausius-Mossotti function, which is similar in form to equation (1) with n^2 replaced by the dielectric constant, ϵ . For polar molecules such as the HCFCs, however, a second term is required on the right hand side of the equation. This term is temperature dependent and it is proportional to the dipole moment. A combination of n and ϵ measurements can be used to determine the dipole moments of these molecules, ref.[5].

Pycnometry, which is the technique of weighing a known volume of a fluid to obtain its density, is also carried out in an optical cell with sapphire windows. We have used this method to measure the density of the saturated liquid and vapor and also the critical density and temperature of R123, ref.[6]. The results are compared with other measurements on this refrigerant in figure 2. There it is seen that all the results agree quite well with a standard deviation of about $\pm 2 \text{ kg/m}^3$ in density.

The speed of sound measurements in the low density gas are particularly useful because their extrapolation to zero pressure allows the calculation of the specific heat of the ideal gas, $C_p^0(T)$, ref[4,7,8], via the relationship,

$$C_p^0/R = 1/(1 - RT/(M u_0^2)) \quad (2)$$

Here u_0 is the speed of sound extrapolated to zero pressure, R the gas constant and M is the molecular weight. As eqn 2 demonstrates, accurate values of C_p^0

require accurate values of both M and u_0^2 . Thus very pure or very carefully analyzed samples are required. Obtaining such samples for alternative refrigerants can be a problem. The specific heat is essential for the construction of thermodynamic tables. It can also be calculated from infrared spectra measurements. However, for complicated molecules such as we have here there are sometimes ambiguities in the assignment of the spectral lines leading to uncertainties in the calculated specific heat. Sound speed can also be used to derive PVT virial coefficients, $B(T)$ and $C(T)$, at low reduced temperatures, a region often inaccessible to conventional PVT measurements due to adsorption problems. Some results of such a calculation for R134a are shown in figure 5. A new acoustic resonator apparatus is under construction, and it will allow measurements to be made at elevated temperatures.

Compressed liquid densities are necessary for calculation of the thermodynamic properties of the liquid phase. We measure them with a vibrating tube densimeter whose resonant frequency is a function of the density of the refrigerant in the tube. Liquid water and vacuum are used as calibration points for the functional relationship. Very precise data may be acquired quite rapidly with this technique. At present the densimeter is thermostated with a water bath which limits the maximum temperature to about 373 K. Measurements have been made at pressures to about 6 MPa, ref.[4,9]. Some results for R 134a, measured by Morrison, are shown in figure 3.

Surface tension, σ , is measured by the capillary rise method in the same cell with the index of refraction prism. It is useful for heat transfer calculations at phase boundaries and also for bubble growth and condensate drainage calculations. Some results for R134a and R123 from Chae, Schmidt and Moldover [10] are shown in figure 4.

The gas-phase PVT apparatus has been described previously [11]. It is

Burnett/isochoric apparatus. P-T data are measured on isochores automatically, under computer control, and the density of each isochore is found from a precise pressure measurement on a baseline isotherm, which has previously been determined by the Burnett expansion method. The heavy nickel sample cell is mounted in a thermostated oil bath, and, although the apparatus has great thermal inertia, data can be acquired continuously with relatively little attention from the operator. Vapor pressures can be measured by filling the cell approximately half full of liquid and measuring the pressure of the two-phase sample as a function of temperature. The accuracy of the pressure measurement is within 2×10^{-4} or 2×10^{-5} MPa, depending on the gauge used, temperature is within 2 mK, and density within several hundredths of one percent. Accuracies at this level are necessary if one wishes to calculate reliable thermodynamic properties.

PVT data. Results are in the form of a two-dimensional network of PVT data for the gas-phase with pressures ranging from 2-40 bar and densities up to about one-half critical. The maximum temperature is about 455 K, and the minimum temperature is determined by the vapor pressure curve. In order to establish experimental precision and to facilitate calculation of thermodynamic properties the data are fit with a virial type equation of state surface,

$$P = RT\rho[1 + B(T)\rho + C(T)\rho^2 + D(T)\rho^3] \quad (3)$$

$$\text{with } B(T) = \sum_0^4 B_i T^i, \quad C(T) = \sum_0^4 C_i T^i, \quad D(T) = \sum_0^1 D_i T^i$$

where $\tau = T^{-1/2}$. This surface fits each set of data with standard deviations less than 0.2 kPa in pressure and 0.02 - 0.03 % in density for all refrigerants studied.

Vapor pressure. The vapor pressure data were fit with an equation of the form

$$\ln P = a/T_c + b + cT_c + dT_c^3 + e(1-T_c)^{1.5} \quad (4)$$

where $T_c = T/T_c$. For each refrigerant the critical temperature T_c was determined with one of our optical cells by observing the disappearance of the meniscus at the critical point. In most cases the vapor pressure can be measured close enough to the critical point so that a short extrapolation of eqn (4) allows us to calculate the critical pressure, P_c .

Results for refrigerants. To date three refrigerants have been studied in the Burnett PVT apparatus, R 134a, ref.[11], R 123, ref.[12], and R 141b. In each case 20-44 vapor pressure data and 50-64 PVT data were measured in the gas phase. The ranges of the data in reduced density and reduced temperature are as follows:

	ρ/ρ_c (max)	T/T_c
R 134a	0.5	0.86-1.13
R 123	0.33	0.78-0.99
R 141b	0.06	0.70-0.82

The R 141b proved to be incompatible with the metal in our apparatus. Slow decomposition was detected at temperatures greater than about 393 K, which accounts for the rather limited range of the data.

Some of the results are illustrated in figures 5-7. Figure 5 shows the virial coefficients for R 134a calculated from eqn. (3). For comparison we have also plotted the values obtained from the speed of sound apparatus, which generally covers a lower temperature range. We see that the second virial coefficients, $B(T)$, determined by both methods are in good agreement, but there is some disagreement for the third virial, $C(T)$. Figure 6 shows the deviations of vapor pressure data, ours and the results of others for R 134a, from eqn.(4). It illustrates very well the precision of our data. Figure 7 is a similar vapor pressure deviation plot for R 123. Again the NIST data are seen to be very precise. For R 141b we were not able to measure vapor pressures near the critical point, due to the compatibility problems. Using a three parameter corresponding states method with two reference fluids, however, as suggested by Teja, Sandler

and Patel [13], we are able to estimate its critical pressure from the relationship

$$\ln P = \ln P_{r,1} + \frac{[\ln P_{r,2} - \ln P_{r,1}]}{[\omega_2 - \omega_1]} (\omega - \omega_1) + \ln P_c \quad (5)$$

where P_r is the reduced pressure P/P_c , and fluids 1 and 2 are the reference fluids, R 123 and R 134a in this case. The accentric factor ω is defined as $\omega = -\log(P/P_c) - 1$ with P being the vapor pressure evaluated at a reduced temperature $T/T_c = 0.7$. Calling the function on the right side in square brackets $f(T_r)$ and using an estimate for T_c of R 141b from index of refraction measurements [2] allows the equation to be plotted as shown in figure 8. At the critical temperature all the quantities $\ln P_r$ equal zero and we obtain a critical pressure of 4.25 ± 0.05 MPa and $\omega = 0.225$ for R141b.

Thermodynamic properties. The thermophysical properties measured in this program provide a very practical basis for the calculation of thermodynamic properties of alternative refrigerants over the range of interest to design engineers. As an example of what is possible by utilizing the data and analytic representations given above, we show in Table I the thermodynamic properties of R123 on the vapor-liquid saturation boundary. For this calculation we use the ideal gas specific heat $C_p(T)$ from the speed of sound measurements (which requires 3 parameters), the virial representation of the gas PVT surface (8 parameters from equation 3), the vapor pressure curve (5 parameters in equation 4), and an empirical representation for the liquid PVT surface (9 parameters). The 25 parameters used allow the precise data to be fit exceptionally well. This is not a global equation of state surface but it does describe the range of conditions required for the design of refrigeration equipment. Here we have set the zero point for enthalpy and entropy as the saturated liquid at 273.15 K.

ACKNOWLEDGEMENTS

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APPENDIX I

Summary of NIST Apparatus for Refrigerants

Automated isochoric PVT apparatus: With manual coupling of isochores by Burnett expansions. Temperatures in the range 0 C to 200 C are measured to 0.002 C. Pressures in the range 1-20 MPa are measured automatically with a resolution of 200 Pa or manually with a resolution of 20 Pa. The vapor pressures of test fluids have been measured with a resolution of 0.01 % from 0.2-5 MPa. Measurements are usually made at densities below the critical density of the test fluid. Within the range of the apparatus, the density of dilute gases is determined with an accuracy of 0.01 %, while the density of compressed gases is determined to 0.05 %. Second virial coefficients have been determined to 0.1 cc/mole.

Ebulliometer: Temperature ranges -30 C to 100 C. The vapor pressures of test fluids are measured in the range 0.01-0.2 MPa by comparing the boiling conditions of the test fluids with the boiling conditions of a standard fluid such as water. The boiling temperature of the standard is controlled and measured to 0.001 K. The vapor pressure of the test fluid is determined with a precision of 0.004 % and an accuracy of 0.01 %, limited by the knowledge of the vapor pressure of water.

Spherical acoustic resonator: Temperature range -40 C to 100 C with pressures to 3 MPa. Materials exposed to sample: brass, stainless steel, aluminum, elastomer O-rings. Used to measure speed of sound in vapor phase with an accuracy of 0.01 % and to obtain ideal-gas heat capacity with an accuracy of 0.1 %.

Spherical acoustic resonator (under construction): Temperature range 100 C to 350 C. Materials exposed to sample at high temperatures: stainless steel. Used to measure speed of sound in gases with an accuracy of 0.01 % and to obtain ideal-gas heat capacity with an accuracy of 0.1 %.

Variable volume sapphire apparatuses: (2) temperature range -5 C to 110 C with pressures to 10 MPa. Coexisting liquid densities are determined with a precision of 0.2 % to 0.5 %, depending upon compatibility with elastomer seals. Coexisting vapor densities are determined with an accuracy of 0.005 g/cc. Pressure and temperature resolution are 0.5 Pa and 0.001 K, respectively. Critical points within the range of the apparatus can be determined to 0.005 K in temperature and 0.2 % in density.

Mechanical oscillator (vibrating tube) densimeter: Temperature range 0 C to 110 C with reduced accuracy from -50 C to 150 C. Pressures to 6.5 MPa (soon to be extended to 15 MPa). Liquid densities near that of water are measured with an accuracy of 0.03 %; an accuracy of 0.1 % is expected for liquid densities far from that of water.

High-pressure continuous dilution dilatometer (under development): Temperature range -5 C to 110 C. Pressures to 5 MPa. Volumes of mixing as small as 0.03 cc/mole are measured. Temperature and pressure resolutions are 0.001 C and 0.05 Pa, respectively.

Differential capillary rise and index of refraction apparatus: Temperature range 0 C to 250 C. Materials exposed to sample: gold, glass, sapphire, and stainless steel. Used to determine critical temperature with an accuracy of 0.005 C, capillary rise with an accuracy of 0.5 ± 0.005 mm and the indices of refraction of the liquid and vapor phases with an accuracy of 0.0003. Measurements are very rapid. If a liquid density datum is available at a single temperature (such as ambient temperature) the Lorentz-Lorenz relation may be used to estimate the coexisting liquid and vapor densities with an accuracy of 1 % or 0.005 g/cc (whichever is larger), and the critical density with an accuracy of 1 %. Systematic density errors on the order of 1 % occur from the failure of the Lorentz-Lorenz relation. The surface tension is determined with an accuracy of about 1 %.

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Table I. Thermodynamic properties of R 123 on the saturation boundary

T K	P MPa	Density kg/m ³	H kJ/kg	S ----kJ/kg - K----	CV	CP
273.15	0.0337	2.31	176.82	.6474	0.59	0.65
273.15	0.0337	1525.93	0.00	.0000	0.59	0.87
300.00	0.0989	6.33	193.01	.6471	0.63	0.69
300.00	0.0989	1459.96	24.49	.0854	0.62	0.95
325.00	0.2258	13.81	207.93	.6525	0.66	0.74
325.00	0.2258	1393.75	49.09	.1638	0.69	1.02
350.00	0.4526	27.07	222.33	.6611	0.70	0.81
350.00	0.4526	1321.38	75.34	.2411	0.75	1.08
375.00	0.8205	49.21	235.84	.6709	0.75	0.89
375.00	0.8205	1240.26	103.17	.3171	0.81	1.14
400.00	1.3753	85.66	247.80	.6798	0.79	1.02
400.00	1.3753	1145.40	132.80	.3923	0.87	1.23
425.00	2.1718	149.15	256.64	.6842	0.85	1.30
425.00	2.1718	1024.59	165.16	.4690	0.99	1.39

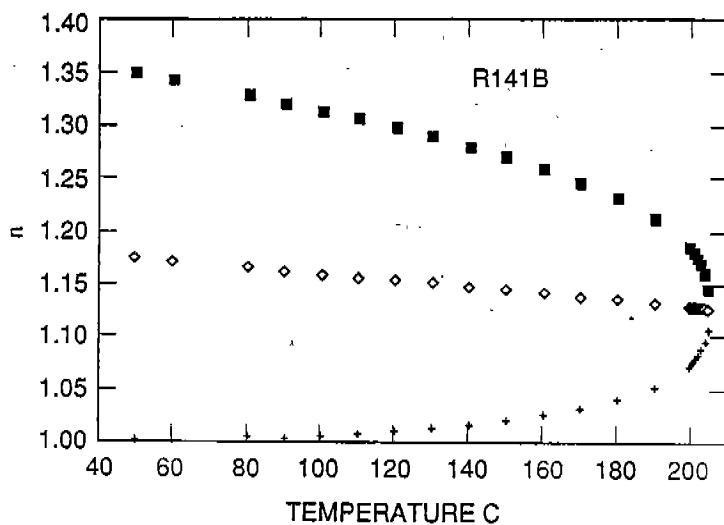


Figure 1. Index of refraction measurements on the saturation boundary of R141b.

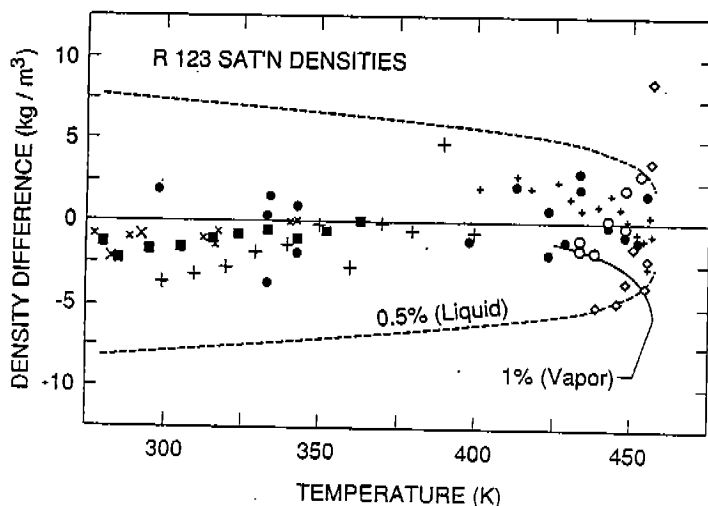


Figure 2. Fit of the saturation densities of R123; circles-pycnometer (filled-liquid, open-vapor), squares-vibrating tube, large X-density balance [14], small x-[16], large cross-[15], small cross-(liquid) [17], small diamond-(vapor) [17]; ----- 0.5 % deviation in liquid phase, ——— 1 % deviation in vapor phase.

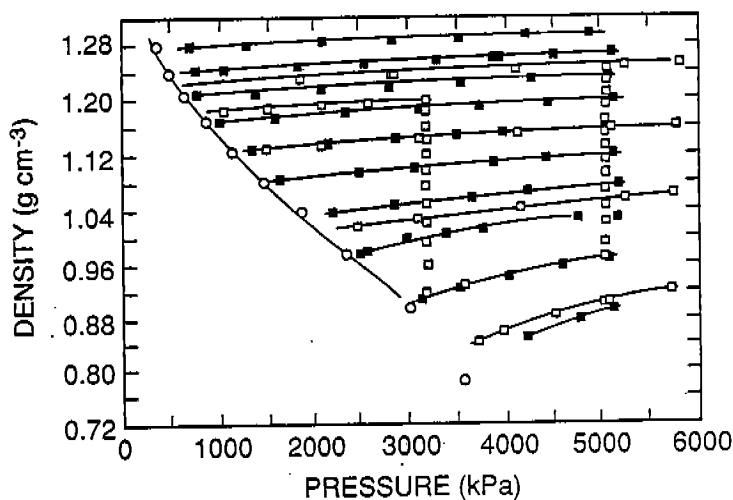


Figure 3. Compressed liquid density data for R134a; lines are isotherms, open circles - saturation boundary.

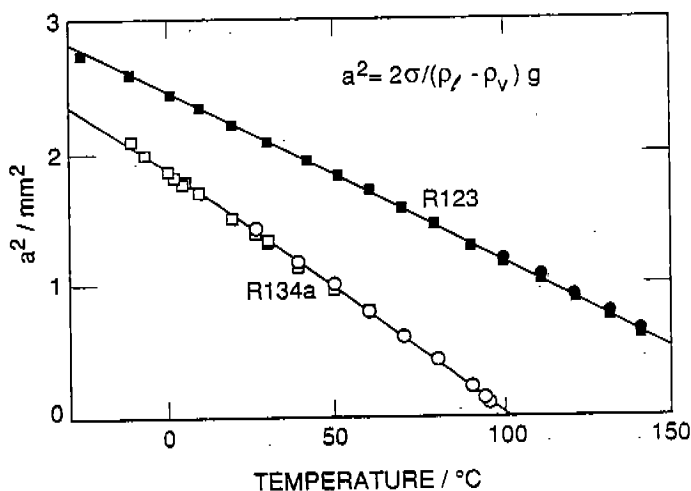


Figure 4. Measurements of the surface tension, σ , of R134a and R123, [10]; ρ_l & ρ_v , saturated liquid and vapor density resp.; g , acceleration of gravity.

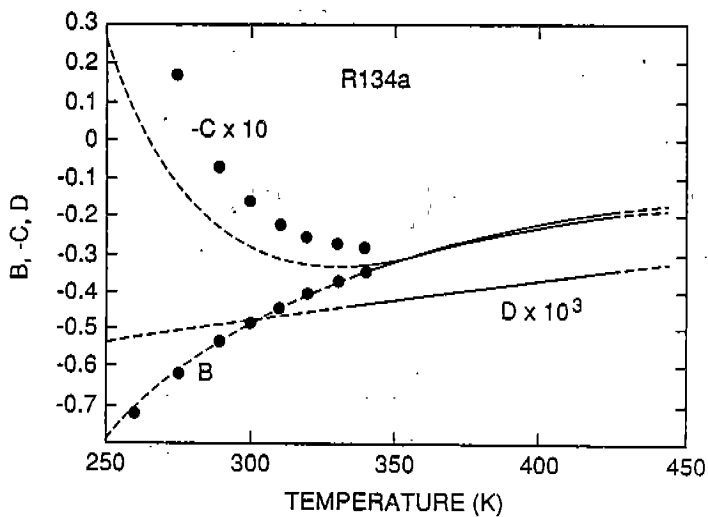


Figure 5. Virial coefficients in eqn. (3) for R134a; dashed lines-extrapolation of PVT data, filled circles-derived from speed of sound data.

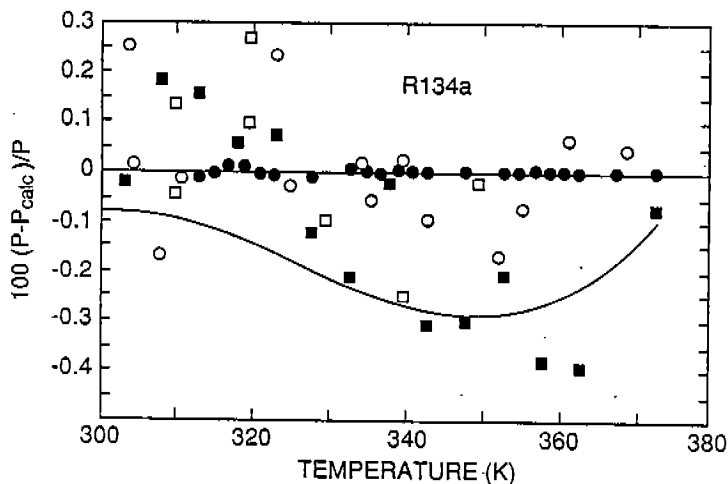


Figure 6. Deviations of vapor pressure data for R134a from eqn. (4); filled circles-this work, open circles-[18], open squares-[15], filled squares-[19], curve-[20].

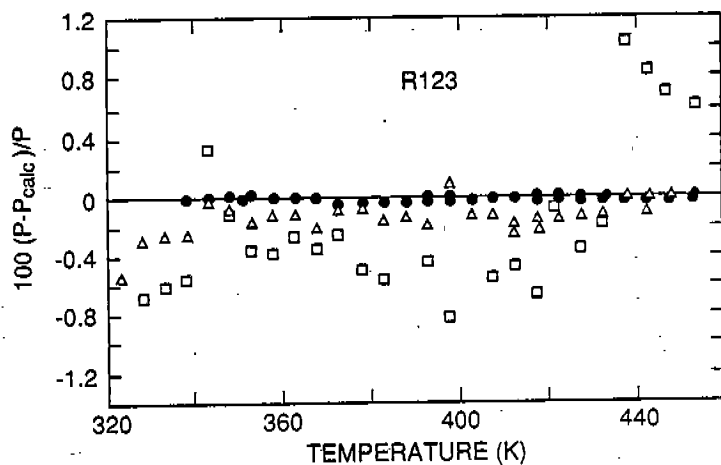


Figure 7. Deviations of vapor pressure data for R123 from eqn. (4); filled circles- this work, squares-[19], triangles-[20].

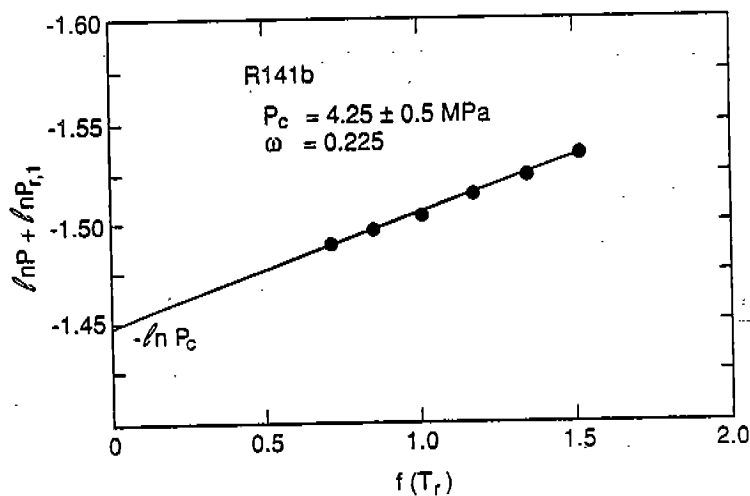


Figure 8. Plot of eqn. (5) to obtain an estimated value of P_c for R141b.